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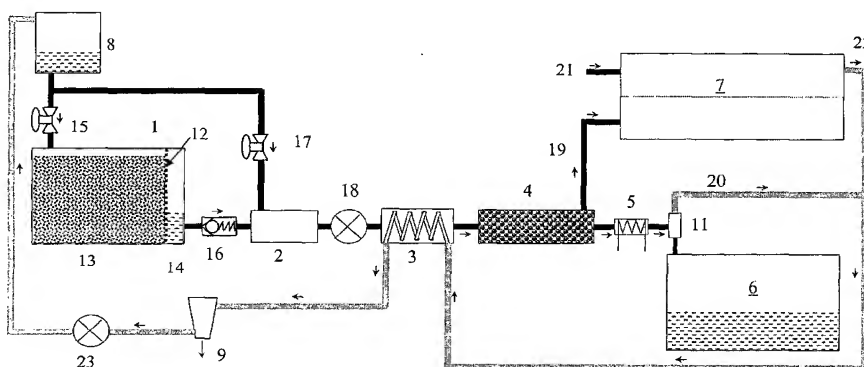
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[Continued on next page]

(54) Title: HYDROGEN FUEL CELL SYSTEMS



(57) Abstract: A hydrogen generation apparatus, in which a hydride is decomposed by a catalyst to produce hydrogen and waste products, comprises: a) a store of solid hydride material; b) dissolution means to dissolve at least part of the solid hydride to produce a hydride solution; c) delivery means to deliver the hydride solution to a catalyst for evolution of hydrogen from the solution and production of a waste solution; and d) waste recovery means to remove waste products from contact with a catalyst.

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## Hydrogen Fuel Cell Systems

This invention relates to fuel cells and is particularly, although not exclusively, related to polymer electrolyte fuel cells.

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A fuel cell is an electrochemical cell that can continuously convert the chemical energy of a fuel and an oxidant to electrical energy. Unlike heat engines, fuel cells are not limited by the Carnot cycle and most of the chemical energy in the fuel may be converted into electricity, typically at an efficiency up to 40-60%.

10

A polymer electrolyte fuel cell, PEFC, is basically a low-temperature electrochemical reactor. It generates electric power by consuming hydrogen as a fuel, and oxygen from air as an oxidant. It has been the most favoured technology by the majority of automotive manufactures due to its high power densities, zero emission potential, mechanical robustness, fast start-up and dynamic response characteristics. The present invention is particularly applicable to PEFC systems but can be used in conjunction with other systems (for example solid oxide fuel cells).

15

Using fuel cells for vehicular propulsion, one of the major issues that has to be solved is hydrogen storage on-board vehicles. A number of potential H<sub>2</sub> storage technologies have been proposed or used. These include:-

20

- use of compressed hydrogen at high pressures;
- use of liquefied hydrogen;
- use of hydrogen adsorption onto metal substrates;
- storage and reforming of natural gas, alcohols and hydrocarbons;
- 25 • use of catalytic reduction of water with metal; and,
- use of slush hydrogen.

25

The US Department of Energy (DOE) has published a Hydrogen Plan calling for a ratio of stored hydrogen weight to system weight of at least 6.5wt% and a volumetric density of at least 30 62kg H<sub>2</sub>/m<sup>3</sup>. Research results published so far indicated that none of these technologies can reach this standard and all have other potential difficulties involving, for example, safety and/or costs.

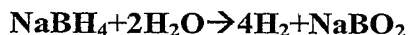
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A much more efficient and low environmental impact H<sub>2</sub> storage technology is needed.

International Patent Application no. WO01/51410 (Millennium Cell, LLC) discloses a hydrogen storage technology using stabilized metal hydride solution as a store for hydrogen in conjunction with a catalyst to release hydrogen from the metal hydride solution. This patent application describes many of the disadvantages to previous storage systems mentioned above. It is also highly relevant towards an understanding of the present invention and is incorporated herein by reference.

The metal hydrides referred to in WO01/51410 are complex metal hydrides and include, for example, NaBH<sub>4</sub>, LiBH<sub>4</sub>, KBH<sub>4</sub>, NH<sub>4</sub>BH<sub>4</sub>, (CH<sub>3</sub>)<sub>4</sub>NBH<sub>4</sub>, NaAlH<sub>4</sub>, LiAlH<sub>4</sub>, KAlH<sub>4</sub>, and mixtures thereof. The present invention is not restricted to these hydrogen-generating materials but is applicable to any hydrogen generating material that can be provided as a solution and that decomposes in contact with a catalyst to generate hydrogen. In the following the invention is described with reference to sodium borohydride, which is a preferred hydride, but the invention is not limited thereto.

Sodium borohydride (NaBH<sub>4</sub>) is a white solid stable in dry air up to temperature of 300°C. It decomposes slowly in moist air or in vacuum at 400°C [Encyclopedia of Chemical Engineering, Fourth Edition, V13, 616-624.]. Sodium borohydride is soluble in many solvents including water. It reacts with water to produce hydrogen (H<sub>2</sub>) and a by-product sodium borate (NaBO<sub>2</sub>):



The uncatalysed reaction is slow, but under catalytic conditions the reaction is relatively fast but smoothly controllable [Schlesinger, H. I., et al., "Recent developments in the chemistry of the boron hydrides", Chemical Reviews, vol 31, 1-41, 1942]. About 4.7kg of NaBH<sub>4</sub> can produce 1kg of H<sub>2</sub>.

Therefore it has the potential to be used as an efficient hydrogen storage medium provided that the following two questions are addressed:

- Does the ratio of stored hydrogen weight to system weight meet technical requirements (e.g. the DOE Hydrogen Plan figure of greater than 6.5wt%)?

- Can the by-product  $\text{NaBO}_2$  be disposed of efficiently and in an environmentally safe manner?

Turning first to generation density,  $\text{NaBH}_4$  has been proposed as  $\text{H}_2$  storage medium for fuel cell applications by a number of researchers. Kaufman et al [Kaufman, C. M., "Catalytic generation of hydrogen from the hydrolysis of sodium-borohydride application in a hydrogen/oxygen fuel cell", Louisiana State University, USA, PhD Thesis, 1981] used acidic catalyst and diluted  $\text{NaBH}_4$  solution. The non-recoverable catalyst was potentially an environmental problem.

Amendola et al (inventors of WO01/51410) used Ru catalyst, but a diluted solution (e.g. <20%) was confirmed to be essential since much higher concentrations (35% or more) leads to clogging of the catalyst by the  $\text{NaBO}_2$  [Amendola, S. C., et al., "An ultrasafe hydrogen generator: aqueous, alkaline borohydride solutions and Ru catalyst", Journal of Power Sources, vol 85, pp186-189, 2000. and Amendola, S. C., et al., "SUV powered by on-board generated  $\text{H}_2$ ", SAE paper 2000-01-1541, 2000.]. The by-product,  $\text{NaBO}_2$ , thus causes problems. Sufficient water is needed to dissolve and remove it from the catalytic reaction bed. Although potentially not harmful to environment, simple release to the environment by the vehicle is certainly not an acceptable solution. It needs to be accumulated and stored on-board vehicle, and by doing so, more water is needed.

Due to the extra weight of the water used for diluting the  $\text{NaBH}_4$  solution, the ratios of stored hydrogen weight to system weight of these existing technologies are much lower than the US DOE requirement. [WO01/51410 calculates efficiencies ignoring the amount of water that has to be carried in solution]:

So a first problem posed by WO01/51410 and other documents relating to the use of  $\text{NaBH}_4$  as a storage medium is, how does one reduce the amount of water present so as to increase hydrogen generation efficiency without clogging of the catalyst?

WO01/51410 describes the use of slurries of  $\text{NaBH}_4$  as a means of preventing the  $\text{NaBH}_4$  from drying out, but the applicants have realised that if the  $\text{NaBH}_4$  can be stored as a solid and prepared as a solution as needed, then the amount of water required can be drastically reduced.

Further, the need for stabilizing agents will be reduced as the solid is likely to be more stable than a solution.

Accordingly, in a first aspect, this invention provides a hydrogen generation apparatus in which a hydride is decomposed by a catalyst to produce hydrogen and waste products, the apparatus comprising:-

- a) a store of solid hydride material;
- b) dissolution means to dissolve at least part of the solid hydride to produce a hydride solution;
- c) delivery means to deliver the solution of hydride material to a catalyst for evolution of hydrogen from the solution and production of a waste solution; and
- d) waste recovery means to remove waste products from contact with the catalyst.

This apparatus also provides the means to solve a second problem in that the waste products may then be delivered to a store for waste products that can then be emptied or removed as appropriate.

Having produced waste products there is the need to dispose of them. The second part of this invention relates to recycling the by-product, for example  $\text{NaBO}_2$ .

Since the discovery of sodium borohydride, two main technologies have been developed and widely used for its industrial production. One is to produce  $\text{NaBH}_4$  from sodium hydride and trimethyl borate in a mineral oil medium at a temperature of about  $275^\circ\text{C}$ . The other process uses finely ground borosilicate glass, sodium, and hydrogen in atmosphere of  $\text{H}_2$  at 300kPa and  $400\text{-}500^\circ\text{C}$ . Although the production rates for both methods are high, these technologies cannot be directly adopted for  $\text{NaBO}_2$  re-circulation.

$\text{NaBO}_2$  is just a simple empirical representation generally accepted for sodium metaborate. It is actually composed of sodium cations and trimeric borate-ring ions in which the boron atom is three-coordinated with oxygen. When a trimeric borate-ring ion is attacked by a highly active negative hydrogen, its electron cloud is shifted so that a new B-H bond is formed and the B-O bond is ultimately cleaved. Therefore, active negative hydrogen provides a means for converting  $\text{NaBO}_2$  back into  $\text{NaBH}_4$ .

The negative hydrogen can be formed from the reaction between hydrogen and metal sodium since sodium is an extremely active electron donor. Alternatively, sodium hydride can be directly used to supply the active negative hydrogen. Unfortunately, these agents are generally unstable and expensive. They are not suitable for wider industrial scale to recirculate NaBO<sub>2</sub> back into NaBH<sub>4</sub>.

Aluminium is relatively active, but inexpensive, stable and safe to handle. It has the potential to be used as the electron donor for the reaction. In this invention, a new method is provided, which can be used to convert waste products into hydrides (e.g. NaBO<sub>2</sub> into NaBH<sub>4</sub>) at industrial scale with relatively low cost.

In the proposed method, instead of reacting Al with H<sub>2</sub> directly, which is relatively difficult to achieve, a chemically active medium such as NaOH is introduced.



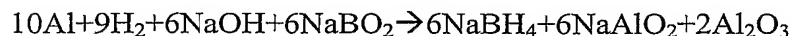
Further aluminium can react with the H<sub>2</sub> to form sodium hydride.



The produced sodium hydride together with the Al and supplied H<sub>2</sub> reduces NaBO<sub>2</sub> into NaBH<sub>4</sub>.



The overall reaction is:



Theoretical investigation shows that the overall reaction is exothermic. No extra external energy sources are necessary. The reaction conditions are generally milder than other methods. Therefore, the overall production can be a relatively economic industrial process. The final products will include NaBH<sub>4</sub>, NaAlO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. NaBH<sub>4</sub> is the required H<sub>2</sub> supplier. The other

by-products,  $\text{Al}_2\text{O}_3$  and  $\text{NaAlO}_2$  are primary aluminium production materials. They can be recycled by aluminium industry.

As can be seen from the above, this process is particularly applicable to the reduction of sodium borates to produce sodium borohydride but the invention is not limited thereto. Accordingly, the present invention provides in a second aspect a method for the production of complex metal hydrides, the process comprising the step of contacting aluminium, a chemically active medium, and a waste product from oxidation of a complex metal hydride under a hydrogen atmosphere.

The chemically active medium may be a hydroxide.

The closed loop of hydride/waste product generation thus results in the overall conversion of aluminium, hydrogen and fuel cell waste products into a hydride for use in a fuel cell; and the conversion of said hydride in a fuel cell into said fuel cell waste products in the fuel cell.

The invention is illustrated in the following description with reference to the attached drawing. Throughout the following reference is made to  $\text{NaBH}_4$  but it is to be understood that other hydrides may be used.

The drawing shows a fuel cell and associated hydrogen generating apparatus. This comprises a hydride storage cartridge 1; a diluter 2; a heat exchanger 3; a catalytic reactor 4; and electric heater 5; a waste storage cartridge 6; a fuel cell 7; a water storage tank 8; a condenser 9; and a steam separator 11.

In operation, water from water storage tank 8 is metered to the hydride storage cartridge 1 via water delivery valve 15.

The hydride storage cartridge 1 is internally separated by a solution permeable membrane 12.

One side 13 of the membrane is used to store the hydride (e.g.  $\text{NaBH}_4$ ) in its solid state, and the other side space is used to contain  $\text{NaBH}_4$  solution. [The  $\text{NaBH}_4$  solution will normally be saturated but as solubility varies with temperature may on occasion become over saturated or under saturated – in the following it will be referred to as saturated  $\text{NaBH}_4$ ]. The saturated



NaBH<sub>4</sub> solution is passed via one-way valve 16 to diluter 2. Flow through the one-way valve is controlled according to the desired H<sub>2</sub> generation rate.

The hydride storage cartridge 1 comprises a water delivery pipe and a solution removal pipe.

5 These pipes may be separate pipes as shown in the drawing or by use of suitable valves can be disposed one within the other so as to provide only a single connection. When disposed one within the other, the water delivery pipe may be inside the solution removal pipe or vice versa as is convenient.

10 Extra water from water storage tank 8 is fed into the diluter 2 via dilution water valve 17 and mixed with the saturated NaBH<sub>4</sub> solution to form a much-diluted NaBH<sub>4</sub> solution ready for the decomposition reaction in catalytic reactor 4.

15 The much-diluted NaBH<sub>4</sub> solution is pumped by pump 18 to pass through the heat exchanger 3 to raise its temperature. Heat for the heat exchanger 3 is provided both by waste water (typically steam) from the fuel cell 7 and by water (typically steam) extracted from the waste products of the hydrogen generator in a manner described below.

20 The heat exchanger 3 both raises the temperature of the diluted NaBH<sub>4</sub> solution (which improves the rate of the decomposition reaction in the catalytic reactor 4), and assists in recovering the water produced from the fuel cell 7 by condensing any steam in its exhaust.

25 High temperature is favourable to the hydrolysis reaction between NaBH<sub>4</sub> and water. Even a slight increase can accelerate the reaction and benefit the H<sub>2</sub> production rate (this dependence upon temperature is discussed in WO 01/51410).

The heat exchanger also serves to reduce the temperature of the exhaust fluid from the fuel cell 7. For reasons given below it is important to condense steam and recover water produced by the fuel cell 7.

30

After passing through the heat exchanger a warmed diluted NaBH<sub>4</sub> solution enters the catalytic reactor 4. The reactor for the hydrolysis reaction between NaBH<sub>4</sub> and water may be coated with Ru catalyst in like manner to WO01/51410. A gas conduit 19 delivers the produced H<sub>2</sub> to the fuel cell 7. A waste outlet passes the exhausted solution to waste (NaBO<sub>2</sub>) storage.

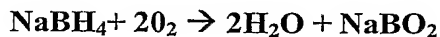
Although the  $\text{NaBO}_2$  could be stored as is, that would be inefficient and have a weight penalty. It is therefore preferred to remove water from the waste solution. Accordingly electric heater 5 is used to heat up the solution and steam separator 10 takes the water vapour produced to leave the  $\text{NaBO}_2$  at saturated condition for storage. The water used to dissolve and remove  $\text{NaBO}_2$  can then be recovered, and passes as steam through reactant waste water conduit 20 for further treatment. Alternative water extraction means can be used (e.g. an osmotic membrane) but a heating step is preferred as this delivers the waste in over saturated condition to the waste storage tank.

The saturated  $\text{NaBO}_2$  is accumulated in waste storage cartridge 6. The temperature of the cartridge is ambient. Therefore, the  $\text{NaBO}_2$  is accumulated on-board at over saturated condition and will precipitate out to form a slush, a slurry, or a wet solid. The parts where saturated  $\text{NaBO}_2$  passes into waste storage cartridge 6 should be arranged so as to prevent precipitation and blockage of the inlet. Heating of these parts may be required.

In the fuel cell 7, which may be any type of fuel cell, although a polymer electrolyte fuel cell is particularly appropriate, hydrogen from gas conduit 19 reacts with air from inlet 21 to produce electricity and, as a waste product, hot water, water vapour, and/or or steam. The hot water, water vapour, and/or steam is removed via fuel cell waste outlet 22. The exhaust fluid from the cell consists mainly of water and nitrogen. The working temperature of a typical PEFC fuel cell is around  $90^\circ\text{C}$  although higher temperatures are possible.

Hot water and/or steam from fuel cell waste outlet 22 and reactant waste water conduit 20 pass through the heat exchanger 3 so heating the diluted  $\text{NaBH}_4$  solution as discussed above. The cooled water then passes to a condenser 9 and is pumped via pump 23 back to the water storage tank 8.

The net reaction of hydrogen generator and fuel cell is:-



and so there is ample water to maintain the system, while surplus water can be released from the condenser 9 to the environment.

Water recovered from both fuel cell exhaust and  $\text{NaBO}_2$  solution is stored in the water storage tank and used to provide a source of water to the hydride storage cartridge 1 and diluter 2 in the manner described above.

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The cartridge 1 may include one or more contents sensors to indicate when the level of  $\text{NaBH}_4$  is below a predetermined level so as to give warning that the cartridge may need replacement. Such sensors may operate on optical, electronic, acoustic or other principles.

- 10 A saturated  $\text{NaBH}_4$  sensor may be fitted between the cartridge 1 and the diluter 2, or preferably in the cartridge 1 itself. Such a sensor can be used to determine the amount of saturated  $\text{NaBH}_4$  ready for delivery and can be used to control water delivery valve 15 as required.

- 15 In the above description the solid  $\text{NaBH}_4$  is provided as a cartridge. Of course, other means of supplying the  $\text{NaBH}_4$  could be contemplated. The  $\text{NaBH}_4$  could be supplied as a loose powder or compressed into a block (in like manner to washing powders).

- 20 The  $\text{NaBH}_4$  may include stabilizing agents to prevent or reduce degradation of the  $\text{NaBH}_4$  from moisture. Such stabilizers are discussed in WO01/51410 but are less likely to be necessary in the present invention as the hydride is stored as a solid.

The waste storage cartridge 6 may be provided with one or more sensors to indicate the contents of the waste storage cartridge 6 and to give a warning of when it needs removal and replacement.

25

In the above, the waste has been shown as passing to a waste storage cartridge 6. Of course, this need not be an actual removable cartridge but could simply be a tank with suitable means being provided to permit washing out of the  $\text{NaBO}_2$  by, for example, hot water.

- 30 Initial theoretical investigation results into the new system show that the system could produce 3.79kg  $\text{H}_2$  with an initial weight of total reactants around 30kg and a final weight around 60kg. In other words, the ratio of stored hydrogen weight to system weight can reach the level of  $3.79\text{kg}/30\text{kg}=12.6\text{wt}\%$ , and the volumetric density is about  $77\text{kg H}_2/\text{m}^3$  or more, which are

equivalent to about 94% higher on weight ratio and 24% higher in volumetric density than the DOE Hydrogen Plan figures.

In contrast the process of WO01/51410, which requires the borohydride to be present as a slurry or saturated solution, would have considerably lower ratio of stored hydrogen to weight and volumetric density for a given borohydride due to the need to store water with the borohydride.

Once the borohydride is produced, it can be sent for recycling by reaction with aluminium and a chemically active medium under a hydrogen atmosphere to reform the  $\text{NaBH}_4$  in the manner described above.

The hydride solution has been shown as pumped to the catalyst. The hydride can also be delivered to the catalyst by passing it to a tank and immersing the catalyst in the tank when hydrogen generation is required (as in WO01/51410). It is preferred however to have a flow of the hydride solution over the catalyst to prevent a build up in waste  $\text{NaBO}_2$  concentration.

The above description has referred throughout to  $\text{NaBH}_4$  as the hydrogen storage medium. Any other hydride with suitable energetics can be used, but  $\text{NaBH}_4$  is preferred both because of its high solubility in water (which reduces water storage needs) and because of the innocuous nature of its waste products ( $\text{NaBO}_2$ ) which reduces the environmental risk of the lifetime use cycle from factory, to fuel cell, and back to factory.

## CLAIMS

1. A hydrogen generation apparatus in which a hydride is decomposed by a catalyst to produce hydrogen and waste products, the apparatus comprising:-
  - 5 a) a store of solid hydride material;
  - b) dissolution means to dissolve at least part of the solid hydride to produce a hydride solution;
  - c) delivery means to deliver the hydride solution to a catalyst for evolution of hydrogen from the solution and production of a waste solution; and
  - 10 d) waste recovery means to remove waste products from contact with the catalyst.
2. A hydrogen generation apparatus as claimed in Claim 1, in which the store of hydride material is adjacent a store for hydride solution.
- 15 3. A hydrogen generation apparatus as claimed in Claim 1 or Claim 2, in which the store of solid hydride material comprises a removable cartridge containing the solid hydride material.
- 20 4. A hydrogen generation apparatus as claimed in Claim 3, in which the cartridge comprises
  - i) a first chamber storing the solid hydride material
  - ii) a second chamber for storing hydride solution
  - iii) a permeable barrier between the first chamber and the second chamber.
- 25 5. A hydrogen generation apparatus as claimed in Claim 3 or Claim 4, in which the cartridge comprises a water inlet pipe and a solution removal pipe disposed one within the other.
- 30 6. A hydrogen generation apparatus as claimed in any preceding Claim, in which the dissolution means comprise:-
  - a) means to deliver water to the store of solid hydride material;
  - b) means to remove hydride solution from the store of solid hydride material;
  - c) a diluter to dilute the concentration of the hydride solution to a desired concentration.

7. A hydrogen generation apparatus as claimed in any preceding Claim, in which the delivery means comprise a heat exchanger to warm the hydride solution prior to delivery to the catalyst.
- 5 8. A hydrogen generation apparatus as claimed in any preceding Claim, in which the waste recovery means comprise water extraction means to remove water from the waste solution.
9. A hydrogen generation apparatus as claimed in Claim 8, in which the water extraction  
10 means comprise means to heat the waste solution and to remove water vapour or steam.
10. A hydrogen generation apparatus as claimed in Claim 9, in which water from the waste recovery means is passed to a heat exchanger to recover heat for heating the hydride solution.
- 15 11. A hydrogen generation apparatus as claimed in any preceding Claim, in which the hydride comprises  $\text{NaBH}_4$ .
12. A hydrogen generation apparatus as claimed in any preceding Claim, in which  
20 stabilizing agents are provided to prevent or reduce degradation of the hydride.
13. A fuel cell system comprising a fuel cell and a hydrogen generation apparatus as claimed in any preceding Claim, in which waste water from the fuel cell is recovered to supply water for the hydrogen generation apparatus and hydrogen from the hydrogen  
25 generation apparatus supplies fuel for the fuel cell.
14. A fuel cell as claimed in Claim 13, in which the waste water from the fuel cell is passed through a heat exchanger to recover heat for heating the hydride solution.
- 30 15. A cartridge adapted for use in a hydrogen generation apparatus as claimed in any of Claims 3 to 5.
16. A method of generating a hydride suitable for use in hydrogen generation apparatus as claimed in any of Claims 1 to 12, comprising the step of contacting aluminium, a

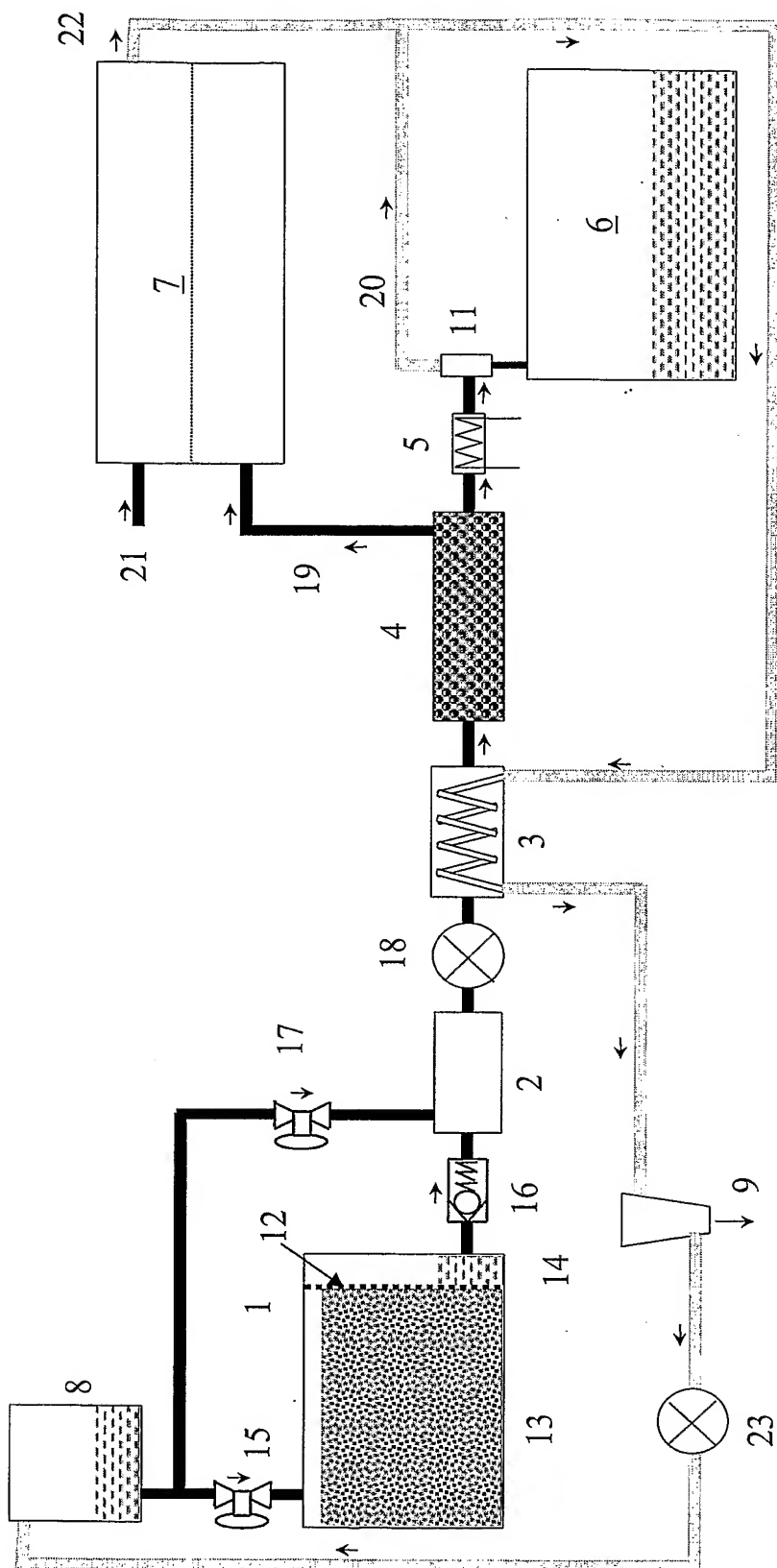
chemically active medium, and a waste product from oxidation of a complex metal hydride under a hydrogen atmosphere.

17. A method as claimed in Claim 16, in which the chemically active medium is a hydroxide.

18. A method as claimed in Claim 16 or Claim 17, in which the waste product from oxidation of a complex metal hydride is a borate.

19. A method as claimed in Claim 18, in which the borate is  $\text{NaBO}_2$ , and the hydride is  $\text{NaBH}_4$ .

20. A method of supplying hydrogen, comprising the steps of supplying a hydride to hydrogen generation apparatus as claimed in any of Claims 1 to 12, recovering waste product from the hydrogen generation apparatus, and regenerating the hydride by the method of any of Claims 16 to 19.





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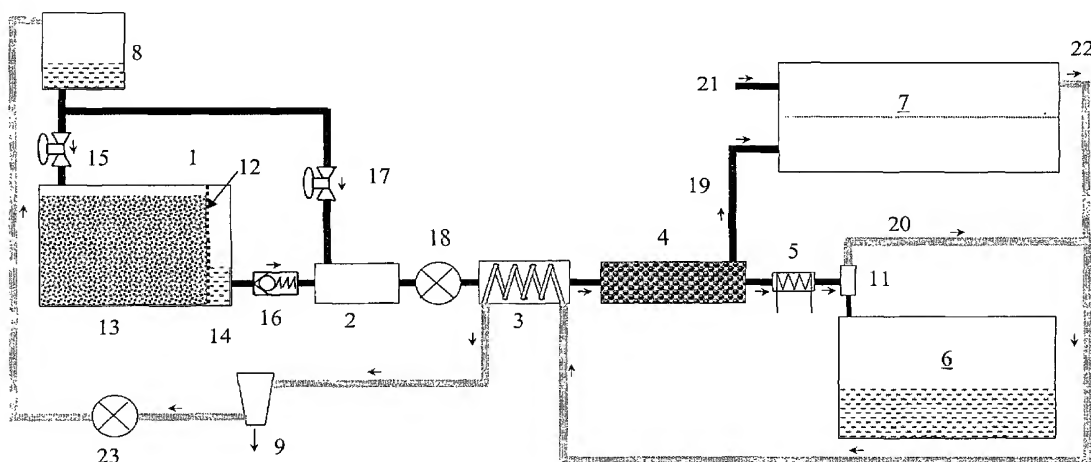
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**Declarations under Rule 4.17:**

— as to the identity of the inventor (Rule 4.17(i)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,

[Continued on next page]

(54) Title: HYDROGEN FUEL CELL SYSTEMS



(57) Abstract: A hydrogen generation apparatus, in which a hydride is decomposed by a catalyst to produce hydrogen and waste products, comprises: a) a store of solid hydride material (1); b) dissolution means to dissolve at least part of the solid hydride to produce a hydride solution; c) delivery means to deliver the hydride solution to a catalyst (4) for evolution of hydrogen from the solution and production of a waste solution; and d) waste recovery means to remove waste products from contact with a catalyst (6).

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IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE,

DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

# INTERNATIONAL SEARCH REPORT

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C01B3/06 B01J8/02 B01J8/00 B01J7/02 H01M8/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 C01B B01J H01M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 170 249 A (TOYOTA MOTOR CO LTD) 9 January 2002 (2002-01-09) paragraph [0004] - paragraph [0006] paragraph [0043] - paragraph [0050] paragraph [0068] - paragraph [0083] figures 1,7-10	1,3,7,8, 13,15
X	US 4 155 712 A (TASCHEK WALTER G) 22 May 1979 (1979-05-22) the whole document	1-4, 13-15
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 29 January 2004		Date of mailing of the international search report 29. 07. 2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Van der Poel, W

## INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/85606 A (STROM OLSEN JOHN OLAF ; UNIV MCGILL (CA); ZALUSKA ALICJA (CA); ZALUSKI) 15 November 2001 (2001-11-15) page 11, line 6 - line 14 page 13, line 22 - page 14, line 11 figure 1 -----	1,3, 11-13,15
A	WO 01/51410 A (AMENDOLA STEVEN C ; MILLENNIUM CELL LLC (US); BINDER MICHAEL (US); KEL) 19 July 2001 (2001-07-19) cited in the application page 5, line 4 - page 8, line 25 page 20, line 29 - page 24, line 5 -----	1,13
A	US 4 261 956 A (ADLHART OTTO J) 14 April 1981 (1981-04-14) column 3, line 21 - column 5, line 54 -----	1,13
P,X	WO 03/084866 A (MILLENNIUM CELL INC) 16 October 2003 (2003-10-16) claims -----	1-3,11, 15

# INTERNATIONAL SEARCH REPORT

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## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-15

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-15

A hydrogen generation apparatus in which a hydride is decomposed by a catalyst, which comprises a store of solid hydride material, dissolution means to dissolve at least part of the solid hydride, delivery means to deliver the solution to the catalyst and waste recovery means. Also included are a fuel cell system including the hydrogen generating apparatus and a cartridge adapted for use with the apparatus.

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2. claims: 16-20

Method for generating a hydride comprising the step of contacting aluminium, a chemically active medium and a waste product from oxidation of a complex metal hydride under a hydrogen atmosphere.

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## INTERNATIONAL SEARCH REPORT

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